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Influence of Promotor, H_2O and H_2S on the Hydrodeoxygenation of Biomass Pyrolysis Vapor over MoS_2 Catalysts

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Introduction

Catalytic hydropyrolysis combines fast pyrolysis with catalytic upgrading by hydrodeoxygenation (HDO) in a single step for the production of fuel oil from biomass in which reactive pyrolysis vapors are upgraded before condensation. Catalyst activity and lifetime is challenged by carbon deposition and by the presence of alkali, nitrogen, sulfur and water. In this contribution, a combined experimental, characterization (in-situ Quick-EXAFS) and theoretical (DFT) study of catalytic HDO of biomass pyrolysis model compounds over MoS_2 based catalysts is presented with emphasis on the influence of water and H_2S.

Materials and Methods

$MoS_2/MgAl_2O_4$ and Co(/Ni)-$MoS_2/MgAl_2O_4$ catalysts with 3.3 wt% Mo and Co(/Ni):Mo molar ratio = 0.3 have been prepared by incipient wetness impregnation and sulfidation with 10-12% H_2S/H_2 at 360-400°C. Ethylene glycol (EG) is a simple model polyol representing the cellulosic fraction of biomass. Catalytic HDO tests were conducted in a fixed bed reactor at 350-450°C, 28 bar H_2 and 545-2200 ppm H_2S (m_{cat} = 0.5-4 g, $feed_{EG}$ = 0.14 mL/min, EG WHSV = 2.3-19 h^{-1}, 40 barg, balance N_2). Products were separated into gas (online analysis by GC/TCD) and liquid (offline analysis by GC-MS/FID). DFT calculations were used to predict the influence of varying H_2O/H_2S ratios on the stability of the sulfide/oxide phases and reaction pathways. The Quantum Espresso code was applied in combination with the BEEF-vdW exchange correlation functional. In-situ Quick-EXAFS was conducted at the SLS SuperXAS beamline [1] at the Co-, Ni- and Mo-K-edge of prepared catalysts during sulfidation and subsequent exposure to varying H_2O/H_2S ratios at 400-450°C. Catalysts and support material have also been analyzed using other techniques such as ICP-OES, NH_3-TPD, XRD, BET and Raman spectroscopy.

Results and Discussion

Co(/Ni)-$MoS_2/MgAl_2O_4$ catalysts were active and moderately selective for EG HDO. 100% conversion was obtained for 50 h on stream at 400°C with 545 ppm H_2S and EG WHSV = 2.3 h^{-1}. At these conditions, a moderate HDO product yield (ethane and ethylene) of 40-45% was observed together with an undesired cracking (C_1: CO, CO_2, CH_4) yield of 30-35%. Catalyst deactivation is believed to be caused by carbon deposition (3.5-9.5 wt% on spent catalysts) and exchange of S by O at the active MoS_2 edges. S-O exchanges may be mitigated with a higher H_2S concentration. In fact, a higher H_2S concentration reactivated and stabilized the catalyst and improved the HDO/cracking selectivity in experiments with EG WHSV = 19 h^{-1}, see Figure 1 (A+B). DFT has however indicated that a too high concentration of H_2S inhibits S-vacancy formation at the MoS_2 S-edge thereby potentially limiting HDO. In-situ Quick-EXAFS has thus been applied to study the effect of varying H_2O/H_2S ratios on catalyst composition. The magnitude of the Fourier Transformed in-situ EXAFS spectra (Figure 1C) shows the transition from oxide (MoO_x) to sulfide (MoS_2) during catalyst sulfidation. The EXAFS fit for the resulting sulfide phase shows contributions from Mo-S (2.40Å) CN = 4.2±0.3 and Mo-Mo (3.15Å) CN = 0.37±0.07. The presence of a small Mo-O contribution (Mo-O (1.61Å) CN = 0.24±0.07) indicates incomplete sulfidation which is possibly caused by interaction of highly dispersed MoS_2 crystallites with the support.

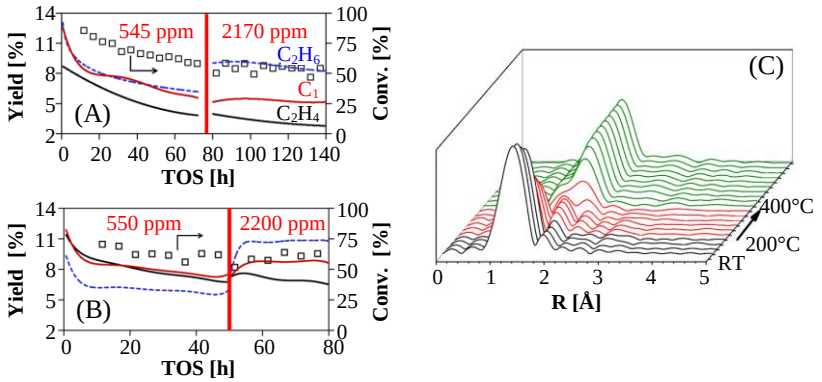

Figure 1 TOS profiles for EG conversion and gas product yields for Ni-$MoS_2/MgAl_2O_4$ (A) and Co-$MoS_2/MgAl_2O_4$ (B) at 400°C, EG WHSV = 19 h^{-1}, 28 bar H_2, 545-2200 ppm H_2S (noted with red text) and total pressure 40 barg. Magnitude of the Fourier Transformed in-situ EXAFS spectra (Mo-K-edge) for in-situ sulfidation (C) of $MoS_2/MgAl_2O_4$ going from oxide (MoO_x, black), through transition phases (red) to a sulfide (MoS_2, green).

DFT calculations have shown that promotion with Ni compared to Co results in more adsorbed H atoms at the S-edge of MoS_2. This higher hydrogen availability could explain the higher yield of ethane compared to ethylene observed for Ni-$MoS_2/MgAl_2O_4$ (Figure 1A). DFT calculations for EG HDO reaction pathways are being conducted.

Significance

To our knowledge, this is the first catalytic HDO study which combines the experimental and theoretical investigation with advanced in-situ XAS characterization to unravel the influence of promotion and H_2O/H_2S on catalytic HDO over MoS_2 catalysts. Understanding the mechanisms behind this influence is a key step in optimizing the catalytic hydropyrolysis process.

References

1. Müller, O., Nachtegaal, M., Just, J., Lützenkirchen-Hecht, D., Frahm, R., J. *Synchrotron Rad.* 23, 260 (2016).